

High Performance PEM Fuel Cells - From Electrochemistry and Material Science to Engineering Development of a Multicell Stack

Interim Report

ONR Contract # N00014-95-1-0114

Submitted by:

**A. John Appleby
Professor and Director
Principal Investigator**

**Center for Electrochemical Systems and Hydrogen Research
Texas Engineering Experiment Station
Texas A&M University System
238 Wisenbaker Building
College Station, Texas 77843-3402**

Submitted to:

**Dr. Lawrence H. Dubois
Defense Sciences Office
Advanced Research Projects Agency
3701 N. Fairfax Drive
Arlington, VA 22203-1714**

**Dr. Robert J. Nowak
Code 313
Office of Naval Research
Ballston Tower One
800 North Quincy Street
Arlington, Virginia 22217-5660**

**Mr. Jay Stedman
10 Harvest Lane
Glastonbury, CT 06033**

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Introduction

The project was proceeding at previous levels of activity until August 1996, with spending at \$32,561.30, \$32,686.62, and \$32,421.17 in June, July, and August 1996, respectively.

The last monthly report was dated July 1996, and was submitted on September 4, 1996. It described work under Tasks 1-3.

Task 1 (MEA Optimization)

Under Task 1, it was shown that apparently identical MEAs of 50 cm² active area with 1.4 mg/cm² Pt./C cathodes (20 wt % Pt on C) and 0.3 mg/cm² Pt/C anodes with 40 μ m thickness Gore-Select™ PEM material did not give identical performance, except in the Tafel region. This indicates that their overall active surface areas at low current density were identical, and that performance suffered at high current density in the range of interest. In all cases, this is shown as a change in polarization slope in the linear region. The slope of the best of these cells was 0.25 Ω -cm², and that of the worst was ca. 0.36 Ω -cm². In consequence, the performance of the best cell at 0.7 V with humidified gases was 0.44 A/cm², and that of the worst was 0.3 A/cm². These are substantially less than 0.7 A/cm² at 0.7 V, which has been achieved in 5 cm² cells. This is the fuel cell performance level required to achieve the overall system performance goals (i.e., 0.7 A/cm² and 0.7 V on hydrogen and air at atmospheric pressure). The variable polarization slope gives the impression of an internal resistance component, but the internal resistance measured at high frequency is rather low, about 0.12 Ω -cm². Thus, the differences in performance observed are either due to problems with the flow-field, or to dispersion in performance between individual MEAs, which otherwise contain identical components made by identical methods.

It has been always noted that performance in 5 cm² cells exceeds that in 50 cm² or larger cells. A number of reasons for this have been identified. PEM electrolytes must contain water to conduct protons, and conductivity increases as the number of water molecules per equivalent (i.e., per sulfonic acid group) increases. There is a limit to this number, which depends of equivalent weight. It also appears to be rather a sharp break between the number of molecules per equivalent at the dewpoint, so that PEM material in contact with just-saturated vapor has lower conductivity than that in contact with liquid water, and unsaturated vapor shows progressively reduced conductivity as vapor pressure decreases. In cells operating under humidified conditions, gases are saturated to give a dewpoint at least equal to that of the cell operating temperature. Product water is therefore liquid, and optimum conductivity is achieved. In contrast, if cells are operated with non-humidified reactant gases close to the dewpoint of the cathode effluent resulting from only product water vapor, the cell will operate, but internal resistance will be higher than when humidified gases are supplied.

In the normal mode of operation with gases humidified either external to the stack, or via humidification membranes or porous plates inside the stack, liquid water may block gas flow channels, particularly on the cathode side. A considerable pressure is required to remove this product water, which generally dictates the use of long, serpentine flow channels, generally in parallel groups. At any given time, a channel or channels may be temporarily blocked. When non-humidified reactants are supplied, the system might in theory operate just at the dewpoint with short channels which have a low resistance to flow. It was felt that this mode of operation could profitably use channels with parallel flow on the anodic and cathodic sides. Co-flow channels would not be expected to operate well, since dry gases would then be present on both sides of the PEM at the inlets of both reactants. This would locally dry the PEM, resulting in high resistance at

that point, which would force the reaction current to the far end of the cell. This would increase current density at the cell exit, obviously giving a lower cell voltage at a given total cell current. Within the cell, conductivity would rely on back-diffusion of product water vapor. This would be an inefficient process. In contrast, counter-flow systems should work well when the reactant gases are not humidified, since product water present in the cathode exit can pass through the membrane to humidify the incoming dry anode stream.

Task 3 (Lightweight Cells Components)

Flow-Fields: Some effort was made under Task 3 to examine flow-field effects, though with humidified gases. A performance comparison of MEAs similar to those described above (although with 1.2 mg/cm^2 Pt/C cathodes rather than 1.4 mg/cm^2) was made with two flow-field configurations, both serpentine with 3 separate channels. The first was in a series configuration, whereas the second was series-parallel. The results described in the last report show 0.43 A/cm^2 at 0.7 V, with a polarization slope of $0.30 \Omega\text{-cm}^2$ for the series-parallel system. Those for the series system show 0.39 A/cm^2 at the same cell potential, with a polarization slope of $0.33 \Omega\text{-cm}^2$. The series-parallel system showed slightly higher performance, and contained some elements of a counter-flow system, whereas the series system is co-flow. Real-time neutron radiography performed at the Texas A&M University cyclotron facility allows the imaging of liquid water formed in any quantity during cell operation. Curiously enough, the series design showed no accumulation of liquid water in the cell channels, whereas some channels in the series/parallel design became plugged almost as soon as cell operation started, and remained plugged throughout the test. This was attributed to uneven gas flow. The implication is that the working channels operated much better in the series/parallel design than those in the series design.

During July-September 1996, a number of approaches to lightweight hardware were examined, and some scale-up of cell designs to $150\text{-}200 \text{ cm}^2$ had been made. It became apparent that little progress in this area could be undertaken until optimized flow patterns could be determined. The introduction to the proposal document for this contract considered that a carbon felt or paper current collector could be used as a flow-field without separate channels. However, our efforts to make MEAs on carbon felt supports show lower performance than those made on graphite cloth with otherwise identical components. In one attempt to simplify the flow-field, a cell was constructed with two flat graphite bipolar plates without flow-channels, with parallel inlet and exit manifolds with low flow resistance. Results obtained were poor, although flow resistance (i.e., pressure drop) was low. Contact resistance was a possible cause, but increased pressure crushed the graphite cloth, cutting off the flow channels and greatly increasing the pressure drop, probably in an irregular manner.

Since serpentine channels with high pressure drop have the best results, it may be hypothesized that a high pressure drop, rather than the exact type of flow-field, is the determining element, since high pressure drop would appear to be necessary to remove liquid water from the flow channels. Accordingly, several experiments were conducted using 2 mm wide flow-channels cut into a 0.8 mm thick grafoil sheets placed on the machined flat graphite cell fixture. Different flow patterns were examined, including interdigitated flow-fields. The grafoil sheets were sufficiently compliant to minimize contact resistance problems. These experiments also gave poor results.

The major problem encountered was the non-uniform nature of the flow-field and electrical resistance field in larger cells. The problem is still under investigation. Clearly, compliant structures are needed to give best results, and mechanical pressures must be both sufficient, and must be uniform. Accordingly, a cell fixture with springs was been constructed, and pneumatic approaches are being examined. The ideal would appear to be the system originally proposed, which would consist of an all-bonded stack. Such a solution must have only a small internal resistance in the bond area. Information solicited from manufacturers of conducting plastic

materials when the present program was planned appeared to suggest that materials with reasonable properties were commercially available.

Metal-Based Structures: To fabricate lightweight bipolar components, metal-based structures were examined. Aluminum bipolar hardware is only in contact with pure water in the PEM, but it is under electric field conditions, and develops a non-conducting oxide film more or less rapidly. Stainless steel and titanium are similar, although their oxide films develop more slowly. Tin oxide should be thermodynamically stable, and it is also conducting. However, the thin corrosion film formed during attempts to use tin-foil also had a resistance which increased with time. All attempts to plate gold, e.g., on to aluminum, gave initially stable results, but the presence of pinholes results in growth of an underlying oxide film, which caused the gold film to peel. Metals therefore did not seem to be a satisfactory solution to bipolar hardware, although after bonding they may make excellent lightweight cooling plates.

Conducting Plastics: We tested a series of commercial conducting plastic products (e.g., from Graphics Technology International, South Hadley, MA) for electrical conductivity through the plane of the material by sandwiching them between two compressed copper plates to simulated a fuel cell contact. The products had proprietary compositions, and consisted of graphite and/or acetylene black with polypropylene or PVC, or apparently in some cases, KynarTM (polyvinylidene fluoride). The products may show good bulk resistivity as measured by a standard method (e.g., 0.26 Ω -cm using ASTM D257 25C, which should give 0.02 Ω -cm² for 0.05 mm, 2 mil, thickness). However, the major problem encountered was the presence of a plastic surface skin with low conductivity, which rendered them unusable. Some could however be sealed between two aluminum foils to give a structure with good conductivity. However, the opposite approach - coating them onto both sides of a single aluminum foil to give an effectively conducting structure, did not prove to be successful. During the 1970s, Alsthom in France, working with Exxon, produced injection-molded graphite-polypropylene bipolar plates for an alkaline fuel cell. The electrodes were bonded to each side of these plates using a conducting epoxy, but the developers claimed that after a suitable surface treatment to reduce skin effects, even small amounts of regular non-conducting epoxy could be used to give a conducting bond with a TeflonTM-bonded electrode. The surface treatment apparently consisted of subjecting the plates to a glow-discharge in air, during which surface plastic decomposed and vaporized. Old Alsthom plates were tested by us for conductivity, but this did not appear to be sufficient, at least based on the surface treatments we attempted. Based on their real bulk conductivity, the ribbed plates were also too thick for use in a fuel cell operating at a current density three times higher than that envisaged in 1975.

Impregnated Graphite Cloth: Another approach examined was the impregnation of the CPW 003 graphite cloth (Textron Specialty Materials, Lowell, MA) used by us as an electrode support. Solubilized NafionTM was chosen as the impregnating material. Non-porous structures could not be made by the methods used. The concept of using NafionTM is of interest, since it will allow product water to pass from the cathode of one cell to the anode of another, which will increase the efficiency of internal humidification. One problem in this case is that an electrolyte (NafionTM) is in contact with an electronic conductor (graphite), which in turn sees anodic and cathodic atmospheres on each side of the bipolar plate. Thus, the possibility that shorted, i.e., kinetically limited, and potentially runaway corrosion or other electrochemical reactions may exist. These could be hydrogen oxidation on the anode side, and oxygen reduction on the cathode side in the next cell, or oxidation of graphite on the anode side, also accompanied by oxygen reduction in the next cell. Graphite is a poor catalytic surface for hydrogen oxidation, but it does corrode when forced to oxygen reduction potentials at high temperature. The latter has sometimes been a problem in the phosphoric acid fuel cell at 200°C. In these cases, when phosphoric acid electrolyte permeates a porous graphite bipolar plate, there is an electronic short circuit between two adjacent cells whose electrolytes are now in contact via a high-resistance pathway, and whose potential differences are equal to the average cell potential. This is a classical corrosion situation. In the

Nafion™ case, graphite corrosion at 80°C will be much less than at 200°C, so perceptible corrosion may not occur. However, if it does, Nafion™ may be replaced by another non-ionic polymer in which water is soluble, e.g., a polyalcohol (for both liquid and gaseous water), or a polyether, polyketone, polyester, or silicone (for water vapor). All of these should be stable under the mild operating conditions in the PEM fuel cell, where they will only contact pure liquid water.

Other approaches: The simple humidification approach used by International Fuel Cells does not even use solid plates, but relies on porous graphite structures with a pore size sufficient to retain liquid water by capillary action, which is then in contact with a deionized water flow-field between the two halves of each bipolar plate. The porous graphite plates act as humidification membranes in regions of the cell where product water formation is reduced, and act as absorbers of liquid product water in regions where product water formation starts to block flow-channels. This can be effected by making a small positive pressure differential between the flow channel and the internal water flow-field, which also serves as a coolant medium via an air-dump radiator. However, this system has two disadvantages. The first is the requirement for pure water in the circulating system, which will require drainage and/or heating when freezing conditions are encountered. The second is an inability to operate the system under dewpoint conditions, where we have shown that if only the anode side is humidified with product water, with the cathode side non-humidified, no significant performance loss at all potentials and current densities of interest occurs compared with the case where both reactant gases are humidified.

Related Work

Department of Energy: By August 1996, it became apparent that approaches to satisfactory lightweight bipolar hardware had yet to be developed.

In June 1996, work started on Department of Energy Contract No. DE -AC08-96NV11985, whose objective is to develop high-activity membrane-and electrode assemblies with low noble metal catalyst loading, with emphasis on ultra-low-loading (0.05 mg/cm² or less) platinum-on-carbon (Vulcan XC-72R, Cabot Corp.) anodes and platinum-base transition metal alloy cathodes (Pt0.5Cr0.25Co0.25 on graphitized Vulcan XC-72R with intermediate loadings, i.e., less than 0.2 mg/cm² expressed as Pt). Performance to be achieved was 0.3 A/cm² and 0.7 V on hydrogen and air at atmospheric pressure. Lightweight cell components were also to be developed.

Since the problems of component development, particularly flow-field analysis and development, were the same in both cases, we decided to considerably slow down spending on ONR Grant Number N00014-95-1-0114, until a satisfactory solution to the problem of lightweight hardware has been determined. In September 1996 spending was reduced to \$20,754.66, and in October, 1996, it was \$11,102.87. Effort was slowed to a very low rate in November 1996 through January 1997, when spending was \$5,839.66, \$5,664.41, and \$5,939.90 respectively, or about 18% of the peak spending rate.

Recent Work: The major disappointment in previous work was the failure to identify suitable conducting plastic materials which would be flexible, non-porous, bondable, inexpensive, and above all, highly electronically-conducting. Bondability, with simultaneous preservation of electronic conductivity across the bonded area can be done, as all experience with the contacts between Teflon™-bonded electrodes and graphite or carbon black layers (e.g., cloth or diffusions layers) has shown. Whether other polymers can be used instead of Teflon™ may be moot, for example we have found that Nafion™ does not bond well to graphite, yet Teflon™ wets graphite at its sintering temperature.

A possible candidate for a bondable plate was grafoil, at least from the viewpoint of conductivity. However, it tends to flake, and is rather porous, allowing gas crossover in cell design approaches other than that of IFC. We have recently examined an interesting material from Carbone Lorraine of France, which is a fairly dense, grafoil-like material which is rendered

impervious via a pyrolytic carbon coating. A 0.2 mm thick planar sample proved to be impervious to hydrogen up to a differential pressure of 16 psig. The weight of this material was 166 g/m², which would be excellent for a lightweight bipolar plate. Its specific resistivity was 0.051 Ω-cm, so that this sample had a surface resistance of only 1 mΩ-cm². Another ribbed sample, which could be used for a cross-flow bipolar plate of conventional construction, weighed 1.2 kg/m². These materials are currently being further examined.

In other work, the cells structure with springs showed that the optimum tie-down pressure for our system was 3 MPa (about 450 psi). Reducing this by about half, or increasing it to twice this amount, reduced the cell potential by about 100 mV in each case.